

Proposal Title: Fullerenes: A New Carrier Phase for Noble Gases in Meteorites

Summary of Research Report

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Summary of Significant Accomplishments- 10/01/00 – 10/31/04

Year-1

The major focus of our research effort has been to measure the noble gases encapsulated within fullerenes, a new carbon carrier phase and compare it to the myriad of components found in the bulk meteorite acid residues. We have concentrated on the carbonaceous chondrites (Allende, Murchison and Tagish Lake) since they have abundant noble gases, typically with a *planetary signature* that dominates the stepped-release of the meteorite bulk acid residue. They also contain an extractable fullerene component that can be isolated and purified from the same bulk material.

Both peer-reviewed published papers and meeting abstracts reported on the findings of non-atmospheric He and Ar in the Murchison and Allende meteorites (Becker et al., 2000, 2001) with $^3\text{He}/^{36}\text{Ar}^*$ ratios that approach the planetary ratio (0.01 vs. a solar ratio of ~ 1) [$^{36}\text{Ar}^* = ^{36}\text{Ar}_m (1 - (40/36)_m / 295.5)$]. In addition, the neon isotopic composition ($^{20}\text{Ne}/^{22}\text{Ne}$) of the fullerene fraction was at or below the atmospheric ratio of 9.8 (~ 8.2 - 8.9) further suggesting that fullerenes are a unique planetary gas carrier as opposed to a solar carrier ($^{20}\text{Ne}/^{22}\text{Ne} \sim 10.5$ - 13.2).

Year - 2

We continued to test our hypothesis that fullerenes rather than other carbon carriers are responsible for the noble gas signatures measured in our extracted meteorite residues by carrying out systematic investigations of the low temperature (100 - 800°C) release of gases from the Tagish Lake carbonaceous chondrite (Pizzarello et al., 2001). Several new measurements were obtained for the fullerene separates that show the release of a “planetary component” at temperatures from 300 - 700°C for Tagish Lake consistent with previous investigations of the Murchison and Allende carbonaceous chondrites. Noble gas ratios ^3He - ^{22}Ne - ^{36}Ar - ^{84}Kr parallel the planetary gas ratios with a $^{20}\text{Ne}/^{22}\text{Ne}$ ratio close to the planetary gas values ($\text{Ne-A} = 8.2$ - 8.9). The ^{36}Ar is $> 95\%$ non-atmospheric ($^{40}\text{Ar}/^{36}\text{Ar} \approx 1$ - 10) and the $^{38}\text{Ar}/^{36}\text{Ar}$ ratio is atmospheric (~ 5.31) also consistent with a planetary signature. The stepped-release curve for the bulk meteorite residue mimics the “pure fullerene” release, providing confirmation that fullerene is likely responsible for the gas release of our meteorite acid residues (Fig.1).

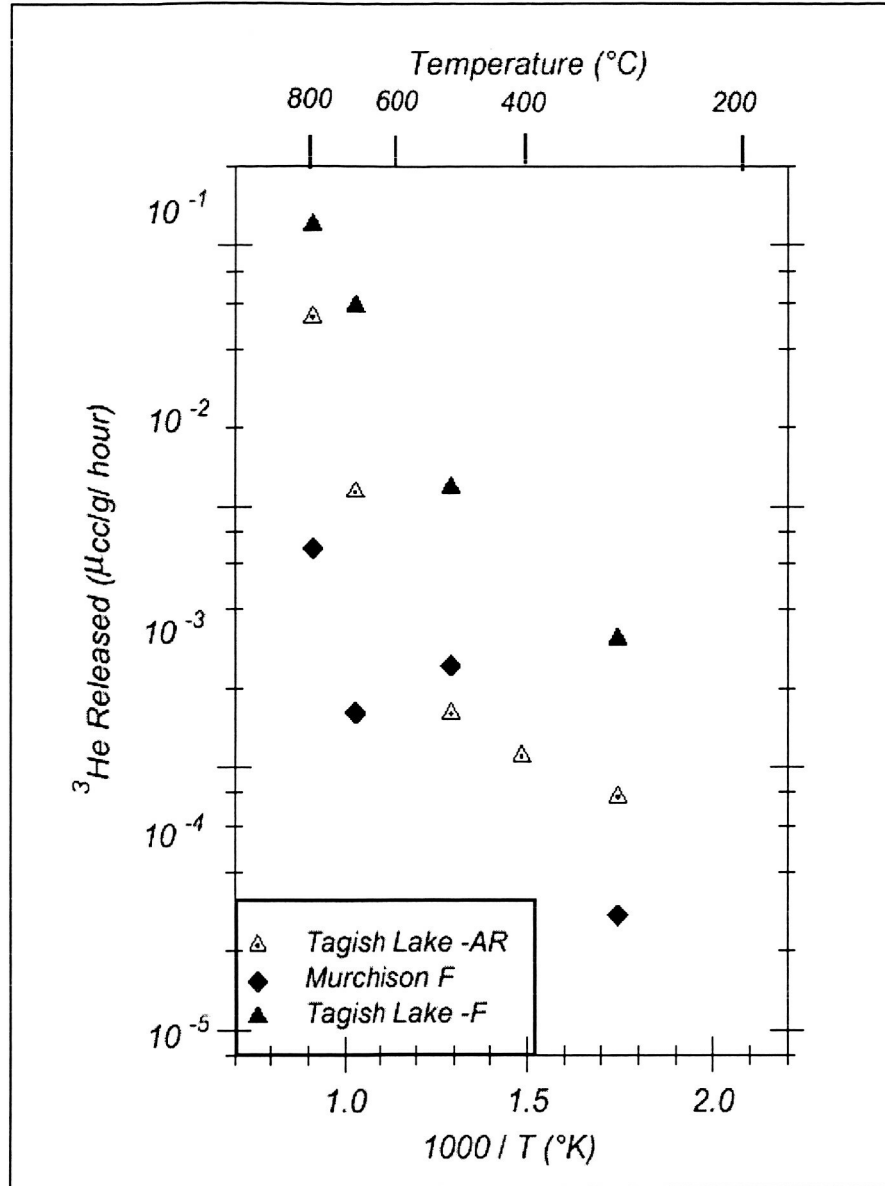


Fig. 1. Temperature (T)-dependent ³He release for the extracted Murchison (solid diamonds) Tagish Lake (solid triangles) fullerenes and the Tagish Lake C-rich acid resistant residue (open triangle with dot). Similar patterns for ²²Ne, ³⁶Ar and ⁸⁴Kr noble gas releases for the Murchison and Tagish Lake fullerenes also trend toward a 'Planetary' pattern as represented by the Tagish Lake C-rich acid resistant residue. The implication is that fullerenes are the carrier of planetary noble gases in carbonaceous chondrites.

Year-3

To further characterize the encapsulation of noble gases in the fullerene cages we started some new experiments on synthetic material “graphitic smokes” in collaboration with Dr. Joe Nuth at NASA Goddard to evaluate the ratios and abundances of noble gases in the larger fullerene cages. Graphitic smokes (GS) are produced by electrically heating a thinned out graphite rod in a noble gas atmosphere (Olsen et al., 2000). The hollow graphite rod allows the C to condense out of the gas more uniformly in comparison to the arc evaporator process used in the synthesis of fullerenes (Kratschmer et al., 1991). Some of these carbonaceous condensates were analyzed for xenon and values as high as $13.7 \times 10^{-6} \text{ cm}^3 \text{ STP/bm}$ of ^{132}Xe were obtained. This is some 2X magnitude greater than typical ^{132}Xe amounts for other synthesized carbonaceous residues (Ott et al., 1981).

We obtained some graphitic smokes synthesized in a noble gas mixture (49% neon, 49% argon, 1% xenon and 1% krypton with the balance of pressure coming from helium) and used our fullerene extraction protocol to determine whether fullerene was a carrier phase for the noble gases measured in the graphitic smoke material. Preliminary measurements of helium and neon in a small amount of toluene extracted graphitic smokes residue (100 μg) indicated that fullerene (C_{60} up to C_{100}) is indeed a carrier phase for the noble gases. Our yield for helium corresponds to one ^4He per 880,000 fullerene molecules and is similar to the abundances measured in synthetic fullerenes produced in the arc evaporator.

The higher fullerenes (up to C_{300}) are also present in the graphitic smokes material however, the dominant cages range from C_{84} to C_{160} and is similar to the Tagish Lake carbonaceous chondrite (Pizzarello et al., 2001). Our extraction methodology for isolation of fullerenes in this size range is extremely robust, thus we should be able to evaluate the encapsulation of the noble gases into individual fullerene cages using the graphitic smokes material. The very efficient trapping of Xe in the graphitic smokes strongly suggests a more significant role for the larger fullerene cages to encapsulate the heavy noble gases. A more complete characterization of the larger fullerene cages may well lead to a better understanding of the nature of planetary atmospheres.

Final Year and Continued Research related to NAG5-11385

Recently, high-resolution transmission electron microscopy studies (HRTEM) have revealed several single and multiple-walled structures interpreted as ‘fullerenic’ closed carbons (see Becker et al., 2005 and refs. therein). These structures are, in general, much larger than the fullerenes we have reported on in some carbonaceous chondrites (Becker et al., 2000; Pizzarello et al., 2001), although some of the single-walled structures may be in the size range of higher fullerenes (i.e. 2-5 nm; a single-layer particle 1.3 nm in diameter is roughly 200 carbon atoms or C_{200}). We decided to look at our extracted residues using HRTEM to determine if indeed the same carbon structures were present in our fullerene-extracted residues.

The GS synthetic fullerene residue identified using LDMS and noble gas mass spectrometry was imaged using HRTEM. The fullerene residue was first dissolved into chloroform and then deposited as a drop of solution onto a lacey carbon film. Upon evaporation of the chloroform, the samples were analyzed using a JEOL 2010 electron microscope operating at 100 kV. The HRTEM of the GS higher fullerene residue (Fig. 2a) revealed several single-walled carbon structures clumped together on the fringe of the

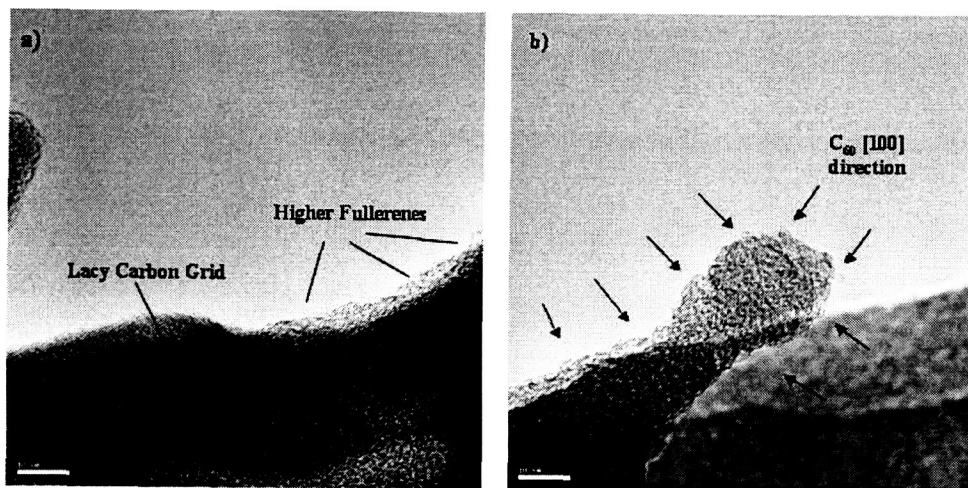
lacey carbon film (i.e. the edge of the film is thin enough to image the fullerenes). The black arrows in the figure indicate discrete structures of the higher fullerenes. Because the fullerene structures are fairly tightly packed it was difficult to get any measurements of the actual sizes of these structures. All of the structures imaged, however in Fig. 2 are larger than the smaller fullerene cages (e.g. C_{60} and C_{70}) since the LDMS spectrum indicates no fullerene $<C_{100}$ are present in the extract (Fig. 1b).

We repeated the procedure used for the GS (TCB) extracted fullerene residue and searched for the smaller fullerene cages observed in our toluene extract. The HRTEM image (Fig. 2b) shows several single-wall structures comparable to the size of C_{60} and some larger closed structures. Interestingly, one of the structures identified appears to be C_{60} viewed in the [100] direction (indicated by the arrow and labeled in the figure). The identification of C_{60} in the GS toluene extract is not surprising due to the very high concentration of C_{60} and other smaller fullerene cages in the LDMS mass spectrum (Fig. 1a). This HRTEM image of C_{60} is also remarkably similar to the calculated images for C_{60} in some flame-generated soots (Becker et al., 2005). The isolated fullerene separates leave no doubt that these single-walled carbon structures observed are the carrier of the noble gases measured in graphitic smokes rather than some other form of carbon (graphite, nanodiamond).

We have also begun to search for single-walled structures in some carbonaceous chondrites including Murchison, Allende and Tagish Lake. The HRTEM image for the Tagish Lake TCB extracted residue (Fig. 3a,b) shows images of small fullerene cages both individual and clusters of fullerenes in the Tagish Lake extracted residue. *To our knowledge, this is the first time that natural fullerenes have been identified in an extracted meteorite fullerene separate.* Both figures show several single-wall structures, some comparable to the size of C_{60} and some larger closed structures. The higher fullerenes tend to cling to one another making it difficult to get measurements on the sizes of the structures although the scale of these images clearly demonstrate the predominance of smaller fullerene cages.

The identification of the higher fullerenes in the GS and Tagish Lake carbonaceous chondrite is definitive proof that the extraction methodology and analytical techniques (e.g. LDMS, noble gas mass spectrometry) we have used uniquely identify fullerenes in natural samples (e.g. meteorites, impact deposits). More importantly, it demonstrates that fullerenes are the carriers of the noble gases we have reported on in the literature (Becker et al., 2000, Pizzarello et al., 2001). The obvious advantage to imaging a discrete phase (i.e. extracted/isolated component) rather than a bulk residue is that the identification of single- or double-walled closed carbon structures can only be fullerenes. *A new Cosmochemistry proposal has been submitted (May 2005) to continue our work on fullerenes and the nature of planetary atmospheres.*

Graphitic Smokes HRTEM 100kV



- 150 Torr He/ 50 Torr NG
- Extracted TMB residue

Fig. 2a,b. High Resolution Transmission Electron Microscopy (HRTEM) images for the toluene and TCB fullerenes in synthetic Graphitic Smokes (Fig. 2a). The fullerene cage sizes in the Fig. 2a image are larger than C₁₀₀ as indicated in our previous investigations of the same material using LDMS and Noble Gas Mass Spectrometry. Fig. 2b. HRTEM image of the toluene fullerene extract of the GS smokes. C₆₀ in the [100] direction can be clearly seen in the image. Scale bar is 10 nm.

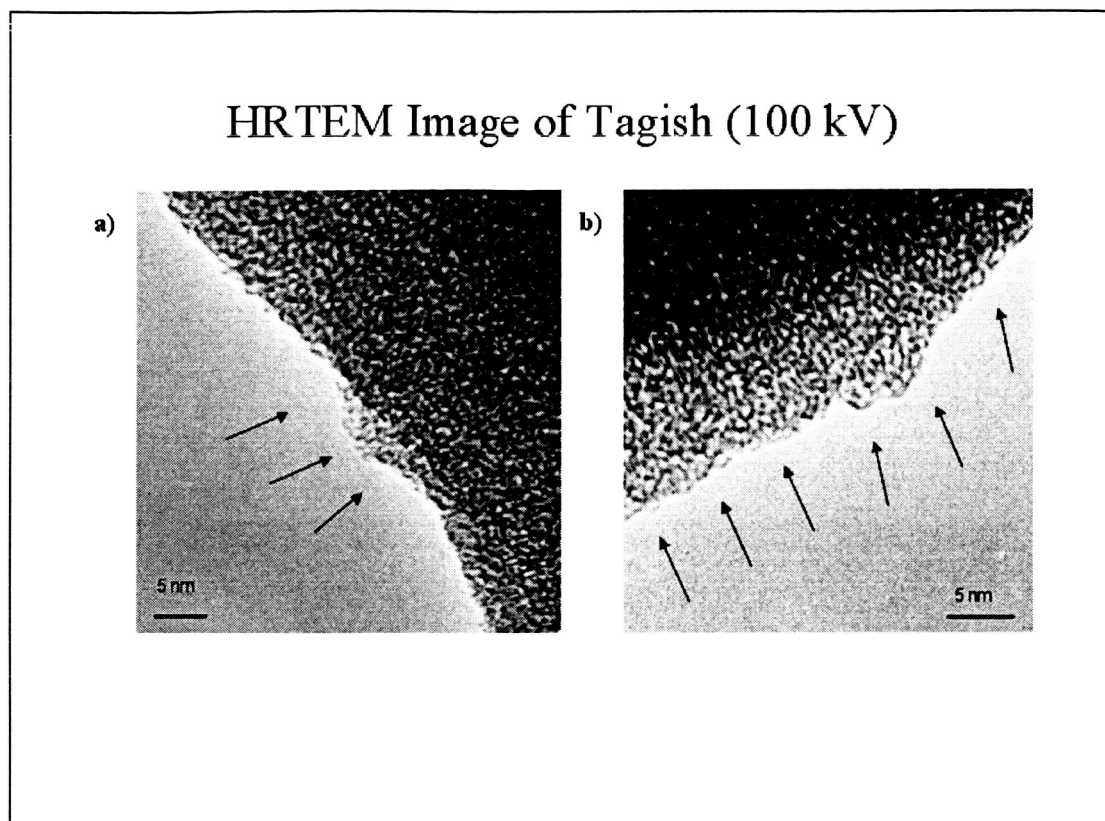


Figure 3a,b High Resolution Transmission Electron Microscopy (HRTEM) images of Tagish Lake fullerenes extracted (TCB) residue. All images were taken using a JOEL 2010 operating at 100kV. The fullerenes are the small circular structures seen in clumps (Fig. 3a) and (Fig. 3b) along the edge of the lacey carbon film. Fullerenes in Tagish Lake are dominated by smaller fullerene cages between C_{60}^{+} and C_{180}^{+} as indicated our LDMS mass spectrum (Pizzarello et al., 2001).

Publication related to NAG5-11385

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